PHOTO-CATALYTIC REDUCTION OF CARBON DIOXIDE OVER ALUMINA DOPED TITANIUM DIOXIDE CATALYST

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ABSTRACT

Carbon dioxide (CO_2) is a major source of greenhouse gas effect which causes the increasing in the Earth's temperature. The continuously increasing CO_2 level into the atmosphere is one of the most serious problems with regard to the greenhouse effect. One of the remediation to overcome this problem by using Photo-reduction process with prepared catalysts assisted by UV light. In this process, CO_2 was converted to methanol (CH_3OH) as a main product. In this study, the influence of the parameters on the catalytic activity with and without visible light irradiation and also effect of percentage of Al_2O_3 loading on TiO_2 were focused. The catalyst was prepared using sol-gel method. The percentage of Al_2O_3 loading on TiO_2 were set in range of 1.50 wt.% - 5.0 wt. %. In photo-reduction process, highly industrial CO_2 was first flowed through NaOH solution with presence of Al_2O_3-TiO_2 catalyst in the reactor. The main product was analyzed using High Performance Liquid Chromatography (HPLC). The results show that for maximum loading of Al_2O_3 into TiO_2 catayst, the performance of photocatalytic activity was enhanced due to the metals will act as electron traps, facilitating electron–hole separation and promote the interfacial electron transfer process. In photo-reduction process, the conversion of CO_2 into methanol was more effective with UV light compared to the process without UV light. As a conclusion, with presence of higher percentage of Al_2O_3 on TiO_2 and UV light, the reduction of CO_2 can be done successfully.

PENUKARAN KARBON DIOKSIDA DENGAN MENGGUNAKAN CAHAYA DAN PEMANKIN ALUMINA DIMUATKN PADA TITANIUM DIOKSIDA

ABSTRAK

Karbon dioksida (CO_2) adalah sumber utama kesan gas rumah hijau yang menyebabkan peningkatan dalam suhu bumi. Peningkatan CO_2 ke atmosfera adalah salah satu masalah yang paling serius dengan mengambil kira kesan terhadap rumah hijau. Salah satu daripada pemulihan untuk mengatasi masalah ini dengan menggunakan proses penukaran dengan menggunakan cahaya beserta pemangkin dan juga cahaya UV. Dalam proses ini, CO_2 telah ditukar kepada metanol (CH_3OH) sebagai produk utama. Dalam kajian ini, pengaruh factor-faktor aktiviti pemangkin dan penyinaran cahaya dan juga kesan peratusan Al_2O_3 pada TiO_2 ditumpukan. Pemangkin disediakan menggunakan kaedah sol-gel. Peratusan Al_2O_3 pada TiO_2 telah ditetapkan dalam julat berat 1.50% -5,0. %. Dalam proses penukaran ini, CO_2 dialirkan melalui NaOH dengan kehadiran Al_2O_3-TiO_2 sebagai pemankin dalam reaktor. Produk hasil dari proses ini dianalisis dengan menggunakan Prestasi Tinggi Cecair Kromatografi (HPLC). Keputusan menunjukkan bahawa untuk memuatkan maksimum Al_2O_3 ke TiO_2, prestasi aktiviti penukaran telah dipertingkatkan kerana logam akan bertindak sebagai perangkap elektron, memudahkan pemisahan elektron dan menggalakkan proses pemindahan elektron ke permukaan. Dalam proses ini, penukaran CO_2 ke metanol adalah lebih berkesan dengan cahaya UV berbanding proses tanpa cahaya UV. Sebagai kesimpulan, dengan kehadiran peratusan yang lebih tinggi Al_2O_3 pada TiO_2 dan cahaya UV, pengurangan CO_2 dapat dilakukan dengan jayanya.

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CHAPTER ONE

INTRODUCTION

1.0 Research Background

The continuously increasing carbon dioxide (CO_2) level into the atmosphere is one of the most serious problems with regard to the greenhouse effect (Slamet, 2009). The increasing of CO_2 is due to our present dependence on fossil fuel. It is due to increasing of demand for energy inevitably. CO_2 is emitted in a number of ways. It is emitted naturally through the carbon cycle and through human activities like the burning of fossil fuels (Jiang, 2010).

The continued increase in CO_2 concentration will cause changes to our global climate. Because it is a greenhouse gas, elevated CO_2 contribute to an additional absorption and emission of thermal infrared in the atmosphere, which produce net warming. This is because CO_2 is a prominent greenhouse gas. It absorbs and emits infrared radiation at wavelength of 4.26 μm that is asymmetric stretching vibrational mode and 14.99 μm bending vibrational mode (Petty, 2004).

It has been shown in many researches it takes longer time for natural removal of CO_2. If we delay about reductions in CO_2 it will cause major problem and the effect of CO_2 emission could be extremely far reaching. There are several methods proposed that can be uses to reduce the concentration of CO_2 due to the increasing of CO_2 such as electrochemical, photochemical, photo reduction and photo electrochemical (Petty, 2004).

In this study, photo-catalytic reduction of CO_2 using catalyst was studied to convert it to valuable product that is methanol. Methanol is a hydrocarbon, comprised of carbon, hydrogen and oxygen. Its chemical formula is CH_3OH. Methanol is an alcohol and is a colourless, neutral, polar and flammable liquid. It is miscible with water, alcohols, esters and most other organic solvents. It is only slightly soluble in fats and oils (Fiedler, 1990).

Methanol has many uses. In the fuel cell application, methanol is widely considered to be one of the most promising fuels for fuel cell applications currently being developed for cell phones, portable computers and small scale transportation such as commuter scooters. Several distinct attributes of methanol make it an ideal hydrogen source for future fuel cell vehicles and may one day provide an alternate source of energy in homes(Wiley, 1985). For the waste water treatment, when wastewater is collected in a treatment facility, it generally contains high levels of ammonia. Through a bacterial degradation process, this ammonia is converted into nitrate. In a subsequent process called denitrification, the nitrate is removed through a combination of chemical treatment and bacterial degradation. Methanol is a simple molecule that serves as an ideal carbon source for the bacteria used in denitrification. Accelerated by the addition of methanol, anaerobic bacteria will rapidly convert the nitrate (NO_3) to harmless nitrogen gas (N_2), which is vented into the atmosphere(Wiley, 1985). In the primary uses of methanol it used as chemical intermediate and fuel. Methanol is used in the production of formaldehyde, acetic acid and a variety of other chemical intermediates which form the foundation of a large number of secondary derivatives. These secondary derivatives are used in the manufacture of a wide range of products including plywood, particleboard, foams, resins and plastics (Wiley, 1985).

In this study, photo-catalytic reduction of CO_2 assisted by UV light in the presence of a catalyst was used as a treatment to produced methanol. In catalyzed photolysis, light is absorbed by an adsorbed substrate to enhance photo reduction activity. The photo-catalytic activity (PCA) depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals for able to undergo secondary reactions (Jeannie, 2012). Prepared Al/TiO_2 catalyst was used in photo-reduction process by using Sol Gel method. Parameters that affect the photo-reduction process were studied. The effect of aluminium oxide loading into titanium dioxide and UV light were investigated in photo reduction reaction. This process is to produce methanol as a valuable produce.

1.1 Problem Statement

Carbon dioxide (CO_2) is a major source of greenhouse gas effect which causes the increasing in the earth's temperature. The concentration of atmospheric CO_2 has increased by about 35 % since the beginning of the age of industrialization. This is due to the globalization and human activities such as the combustion of fossil fuels and deforestation. In order to overcome this problem, the researchers work hard to find the best remediation for this matter. Due to this problem, one of the best methods was introduced by using photo-reduction process with prepared catalysts by using Sol Gel method assisted by UV light. The sol-gel process is a wet-chemical technique widely used in the fields of materials science and ceramic engineering. CO_2 as a waste product were converted to valuable product that is methanol. Methanol became important product because it has many uses especially as fuel cell application.

1.2 Objectives

Based on the research background and problem statement described in the previously, the objectives of this research are as follows:

- To synthesize photo-catalyst, Al_2O_3-TiO_2 that used in photo-reduction process of CO_2.
- To study the performance of the prepared catalysts and the influence of the parameters on the catalytic activity.

1.3 Scope of Study

In order to accomplish the objectives of this research, the following scopes were drawn:

- Synthesizing the photo-catalyst by doping Al_2O_3 on TiO_2 catalyst by using sol gel method. In sol gel method, the catalyst were prepared in powder form.
- The effect of loading of Al_2O_3 into TiO_2 was studied in the range of 0.50 -5.0 wt. % of Al_2O_3 on TiO_2. The effects were measured by analyzed methanol produce.
- Photo-reduction process was studied with and without UV light to see the effect of UV light on yield of methanol in photo-reduction process Main product (methanol) was analyzed by using High-performance liquid chromatography (HPLC).

1.4 Organization of Thesis

This report contains five main chapters to distribute the whole report accordingly. In the first chapter, explained the introduction which gave the briefing about the project. In the first chapter also contain problem statement, objective and scope of study. The second chapter contains literature review which is based on photocatalytic reaction and preparing aluminum-titanium dioxide catalyst. The review in this chapter were made from the studied of researcher from all over the world. The third chapter explained the methodologies of the experiment. The constant value and standard curve preparation were shown in this chapter. The fourth chapter contained results and discussions. The result obtained from this studied were illustrated in table and chart form. The result obtained were discussed and compared with other research result. Finally, fifth chapter contains with conclusions and recommendations. The conclusion were made to support objective of this studied whether the result obtained is achieve the goal of this studied. The recommendation was made to give addition information for the further studied on this topic to get better result and for expending the studied on this topic.

CHAPTER TWO

LITERATURE REVIEW

2.0 Introduction

Carbon dioxide (CO_2) is one of the gases in our atmosphere, being uniformly distributed over the earth's surface at a concentration of about 0.033% or 330 ppm (Shakhashiri, 2008). CO_2 is released into our atmosphere when carbon-containing fossil fuels such as oil, natural gas, and coal are burned in air. As a result of the tremendous world-wide consumption of such fossil fuels, the amount of CO_2 in the atmosphere has increased over the past century, now rising at a rate of about 1 ppm per year. Major changes in global climate could result from a continued increase in CO_2 concentration (Shakhashiri, 2008).

Beside that, CO_2 has increased in the atmosphere from fossil fuel use in industry and transportation, manufacture of cement, building air conditioning and deforestation. With a global radioactive forcing of 1.74 $W.m^{-2}$, CO_2 is the largest contributor among well-mixed long-lived greenhouse gases, accounting for more than 63 % of the total (Richter, et al., 2011). CO_2 is a greenhouse gas as it transmits visible light but absorbs strongly in the infrared and near-infrared, before slowly re-emitting the infrared at the same wavelength as what was absorbed. The resulting accelerating accumulation of CO_2 in the troposphere, with projections of continued warming in the absence of resolute changes in CO_2 management and this will cause the greenhouse effect with a significant atmospheric temperature rise and which will produce net warming (Revkin, et al., 2000).

In Malaysia, the emissions of CO_2 also occur. There are many factors that affect the emissions of CO_2.Electricity generation, transportation, industrial and residential are the main sectors identified to contribute to the emission of CO_2 in Malaysia. It was projected that without any mitigation measures being taken up by the country, 285.73 million tonnes of CO_2 will be released in 2020, which is a 68.86% increase compared to the amount of CO_2 emitted in year 2000. Electricity generation, which gives 43.40% out of total of emissions, was discovered to be the largest emitting sector among all sectors (Nor Sharliza Mohd Safaai, 2010). From **Figure 2.1** and **Figure 2.2,** total CO_2 emissions represent the mass of CO_2 produced during the combustion of solid, liquid, and gaseous fuels. Carbon dioxide emissions are often calculated and reported to see the emission of CO_2 in our atmosphere. The trend of CO_2 emission is increasing by year. From year 1970 until 2010, the differences between those years are really large due to development of industry sector in our country. This increasing of CO_2 is serious problem because it has many effects to our environment and our health.

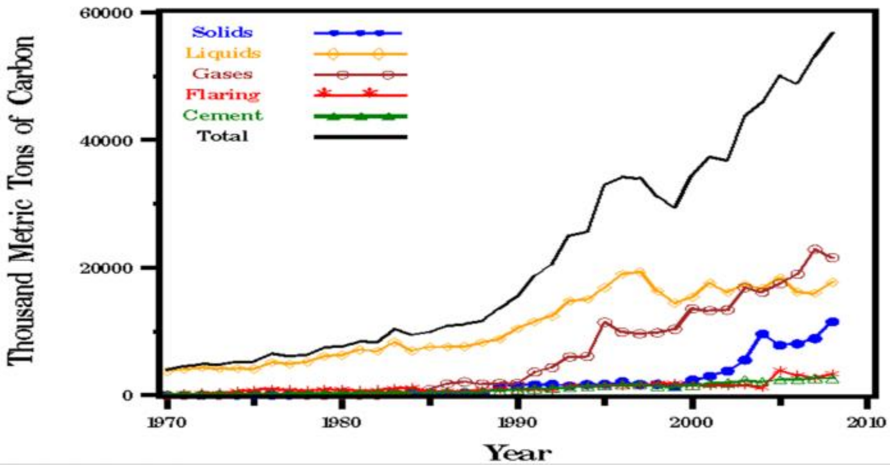

Figure 2.1: CO_2 emission from Malaysia(http:wwwcdiac.ornl.gov)

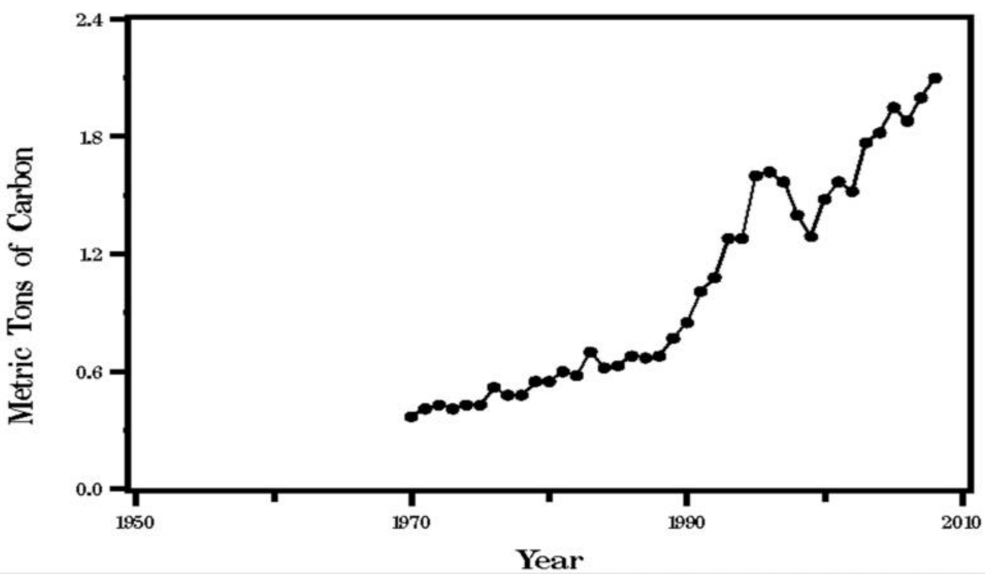

Figure 2.2: CO_2 emission estimates for Malaysia (http:www.cdiac.ornl.gov)

2.1 Photo Reduction Process of Carbon Dioxide (CO_2)

Photo reduction may be termed as a photo induced reaction which is accelerated by the presence of a catalyst. These types of reactions are activated by absorption of a photon with sufficient energy that is equals or higher than the band-gap energy of the catalyst. The absorption leads to a charge separation due to promotion of an electron from valence band of the semiconductor catalyst to the conduction band, thus generating a hole in the valence band. The recombination of the electron and the hole must be prevented as much as possible if a photo-catalysed reaction must be favoured. The ultimate goal of the process is to have a reaction between the activated electrons with an oxidant to produce a reduced product, and also a reaction between the generated holes with a reductant to produce an oxidized product (Hameed, et al., 2009).

Photo-catalytic reduction process is a method that can be used to reduce the concentration of CO_2 by using photosensitive semiconductor materials such as TiO_2, ZnS, ZrO_2, V_2O_5, ZnO, CeO_2 and NbO_5 as photo-catalysts. Hoffman (1995) was reported about TiO_2 in photo-reduction process that TiO_2 has been widely studied for its application as photo-catalyst because of its excellent stability and strong oxidizing property. However, TiO_2 is a wide band gap semiconductor with 3.03 eV for rutile and 3.18 eV for anatase and can only absorb about 5 % of sunlight in the ultraviolet region, which limits its photo-catalytic activity (Hameed, et al., 2009).

Mishra et al.,(2007), reported in his study that the photo-catalytic activity is strongly dependent on the electro-optical properties of the photo-catalyst, defects removal, particle size and specific surface area. Therefore different modified TiO_2 were also used to improved catalytic reduction.

Photo-catalysis has recently become a common word and various products using photo-catalytic functions have been commercialized. Among many candidates for photo-catalysts, TiO_2 is almost the only material suitable for industrial use at present and also probably in the future. This is because TiO_2 has the most efficient photo-activity, the highest stability and the lowest cost. More significantly, it has been used as a white pigment from ancient times, and thus, its safety to humans and the environment is guaranteed by history. There are two types of photochemical reaction proceeding on a TiO_2 surface when irradiated with ultraviolet light. One includes the photo-induced redox reactions of adsorbed substances, and the other is the photo-induced hydrophilic conversion of TiO_2 itself (Kazuhito, et al., 2005).

In this process, UV light is used because it can enhance the process. It can increase the efficiency of the process by reduce the reaction time (Azmi, 2005). However, TiO_2 exhibits a relatively high energy band gap that is 3.2 eV and can only be excited by high energy UV irradiation with a wavelength shorter than 387.5 nm. Efforts have been made to extend the light absorption range of TiO_2 from UV to visible light and to improve the photo-catalytic activity of TiO_2 further by adding metals such as silver, cooper, alumina and other (Wu, et al., 2005). In this experiment, alumina was used to dope on TiO_2 as a catalyst for this reduction process.

The main purpose of this study to reduce the emission of CO_2 to atmosphere hence to produce valuable product such as methanol and the main reaction was shown in Eq. (2.1),

$$CO_2 + 2H_2O \xrightarrow{UV} CH_3OH + 3/2\, O_2 \qquad (2.1)$$

The efficiency of photo reduction of CO_2 with H_2O is one of the most challenging tasks of environmental catalysts because titania is a photo-excited catalyst. The band gap of anatase form TiO_2 is 3.2 eV, making it a perfect candidate for UV illumination (Wu, 2005).

2.2 Materials Used as a Catalyst in Photo-Reduction Process

2.2.1 Alumina (Al_2O_3)

Aluminium is the most abundant metal and the third most abundant element in the earth's crust, after oxygen and silicon. It makes up about 8 % by weight of the earth's solid surface. Aluminium is too reactive chemically to occur naturally as the free metal. Instead, it is found combined in over 270 different minerals. The chief ore of aluminium is bauxite, a mixture of hydrated aluminium oxide ($Al_2O_3 \cdot H_2O$) and hydrated iron oxide ($Fe_2O_3 \cdot 2H_3O_6$). Another mineral important in the production of aluminium metal is cryolite (Na_3AlF_6). However, cryolite is not used as an ore; the aluminium is not extracted from it (Shakhashiri, 2008).

Meor Yusoff and Masliana, (2007) were defined alumina (Al_2O_3) as a white powder that normally produced from bauxite ores. It is one of the most widely used advanced ceramic materials with applications ranges from spark plugs to catalyst materials. Al_2O_3 attractive for engineering applications due to its chemical and thermal stability, relatively good strength and electrical insulation characteristic combined with availability in abundance have made. Other than that, it is also a relatively low cost material, and by using a number of fabrication methods, it can easily be formed and finished. Al_2O_3 has several allotropic forms, but only the usual type or α-alumina is considered. It has an internal crystal structure where the oxygen ions are packed in a closed packed hexagonal (cph) arrangement with aluminium ions in two-thirds of the octahedral sites. Tshang et. al., (1979) stated that Al_2O_3 have a high quality optical and di-electric properties and therefore suitable for antireflection coatings on a semiconductors.

2.2.2 Titanium Oxide (TiO_2)

Titanium dioxide (TiO_2) or titania is a very well-known and well researched material due to the stability of its chemical structure, biocompatibility, physical, optical and electrical properties. It exists in four mineral forms that are anatase, rutile, brookite and titanium dioxide (B) or TiO_2(B). Anatase type TiO_2 has a crystalline structure that corresponds to the tetragonal system (with dipyramidal habit) and is used mainly as a photo-catalyst under UV irradiation. Rutile type TiO_2 also has a tetragonal crystal structure (Rajalakshmi, 2011). This type of titania is mainly used as white pigment in paint. Brookite type TiO_2 has an orthorhombic crystalline structure. TiO_2(B) is a monoclinic mineral and is a relatively newcomer to the titania family. TiO_2, therefore is a versatile material that has applications in various products such as paint pigments, sunscreen lotions, electrochemical electrodes, capacitors, solar cells and even as a food coloring agent and in toothpastes. The possible application for this material as a photo-catalyst in a commercial scale water treatment facility is due to several factors. Firstly, the photo-catalytic reaction takes place at room temperature. Secondly, photo-catalytic reactions do not suffer the drawbacks of photolysis reactions in terms of the production of intermediate products because organic pollutants are usually completely mineralized to non-toxic substances such as CO_2, HCl and water. Thirdly, the photo-catalyst is inexpensive and can be supported on various substrates such as, glass, fibers, stainless steel, inorganic materials, sand, activated carbons (ACs), and allowing continuous re-use. Lastly, photo-generated holes are extremely oxidizing and photo-generated electrons reduce sufficiently to produce superoxides from dioxygens (Rajalakshmi, 2011).

Besides that, TiO_2 is widely used in many photo induced processes because of its comparatively low cost, low toxicity and its ability to resist photo-corrosion. The effect of transition metal ion on TiO_2 was studied for CO_2 photo-reduction. Addition of metal to TiO_2 can change the distribution of electrons and they prevent the electron hole recombination, thereby enhancing the photo-catalytic efficiency of TiO_2 (Rajalakshmi, 2011).

Titanium Oxide (TiO_2), as a wide-band gap energy semiconductor, has been intensive and in-depth studied on coprecipitation, impregnation, and method improvement to obtain the useful materials for photo-electrolysis of water, photo-catalytic degradation of toxic organic and inorganic contaminants , and some of catalytic reaction. By using solid-state reaction aluminum oxide had been doped into the framework of anatase TiO_2 to form alumina-doped titania (Al_2O_3-TiO_2). The mesoporous Al_2O_3-doped TiO_2 material, not only possessed high thermal stability hexahedral mesostructure, large surface area and narrow distribution of pore size, but also showed excellent photo-degradation behavior (Liu et al., 2009).

2.3 Method in Preparation of Heterogeneous Catalyst

2.3.1 Sol Gel Method.

Nowadays, sol gel method have become very popular recently due to their high chemical homogeneity, low processing temperatures, and the possibility of controlling the size and morphology of particles. Sol gel provides excellent matrices for a variety of organic and inorganic compounds when the material is derived. One of the most important features of this method is its ability to preserve the chemical and physical properties of the dopants. Thus, make it as unique hosts for a biologically important molecule which can be apply in biomedical aspects (Subramanian, et al., 2008).

Sol–gel is one of the most exploited methods. It is used mainly to produce thin film and powder catalysts. Many studies revealed that different variants and modifications of the process have been used to produce pure thin films or powders in large homogeneous concentration and under stoichiometry control(Akpan and Hameed, 2010).

Based on Akpan and Hameed(2010), the doping TiO_2 with transition metal ions usually resulted in a hampered efficiency of the TiO_2 catalyst, though in some few cases, enhancements of the photo reduction activity of TiO_2 were recorded by doping it with some transition metal ions. In most cases, co-doping of TiO_2 increases the efficiency of its photo reduction activity. Based on their review reveals that there are some elemental ions that cannot be used to dope TiO2 because of their negative effects on the photo reduction activity of the catalyst, while others must be used with caution as their doping will create minimal or no impacts on the TiO_2 photo reduction efficiency(Akpan and Hameed, 2010). **Figure 2.3** shows the flow preparation of catalyst with doping Al_2O_3 into TiO_2 by using Sol-Gel method. The process are aimed to added

Al_2O_3 into TiO_2 based catalyst. The process beginning with Al_2O_3-TiO_2 mixture were alcoholate and then added with acidifying reagent to perform gel. The process of gel performing is called sol gel process. Finally the sample is drying and calcination.

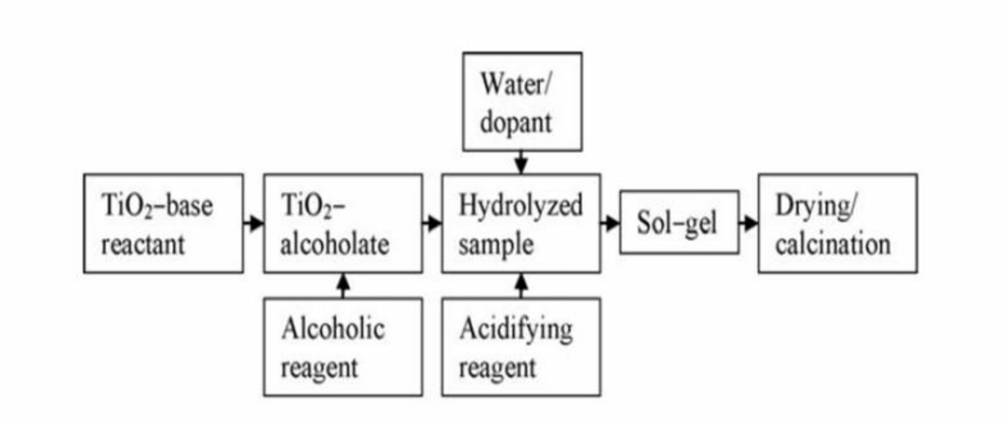

Figure 2.3 : Process flow chart for the preparation of TiO_2-based catalysts by sol–gel method(Akpan and Hameed, 2010).

2.4 Parameters that affect the photo reduction process

There is many parameter that affect the photo reduction process. In this studied, the concern are only the effect of UV light and the effect of Al loading on TiO_2

2.4.1 Effect of UV light

There is many research of effect UV light in photo reduction process. Mohsen Padervand et al. reported that due to the wide band gap of TiO_2 (3.0-3.2 eV), it is active only under near ultraviolet irradiation(Mohsen Padervand et al 2011). Chih Ming Ma et al. reported that in the reaction process of UV/TiO_2 , an electron-hole pair is generated after TiO_2 has been exposed to ultraviolet light (UV) with a wavelength (λ = 365 nm) in the near visible spectrum. The electrons then reduce the heavy metals and this is the reduction path. The hole generates the free radical through a series of reactions, and then organic matters are oxidized into carbon dioxide and this is the oxidation path. However, a shortcoming of this process is that the electron-hole pair may be bound again, thus decreasing the efficiency of the photo reduction. Hence, the addition of an organic hole scavenger enhances the photo reduction effect. Generally, organic holes scavengers comprise organic compounds such as methanol, ethanol, formic acid, and acetic acid (Chih. Ming Ma et al. 2012).

2.4.1 Effect of Al loading on TiO_2

The effects of metal loading on TiO_2 catalyst are interesting topic because it is the way to improve the catalyst activity. These effects have been theoretically described as an increase in local electromagnetic field nearby metal surfaces which is found when the wavelength of the irradiation sources are correlated with the optical absorption of the surface plasma on resonance (C. Photiphitak, et al. 2010). Shaoyou Liu et al. reported from his study show that the photo reduction activity are better with Al doped into TiO_2 than undoped $TiO_{2.}$ He claimed that the phenomenon is due to the macrostructure of Al-doped TiO_2 which is that was the results from the modification of the electronic energy band structure of TiO_2 through the doping of Al element (Shaoyou Liu et al, 2010). It also has been reported that the conductivity of the Al-doped TiO_2 is higher than that of pure TiO_2 in a temperature range of 600–900 ◦C. Since ionic radii for Al and Ti are close to each other (0.074 nm for Ti^{4+} and 0.0675 nm for Al^{3+}), Al can occupy a regular